

Lithium Deintercalation from the O2-LiCoO₂ Phase: Structure and Physical Properties

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The O2-type LiCoO₂ phase was obtained for the first time 20 years ago in our laboratory by Li⁺/Na⁺ exchange from P2-Na_{0.70}CoO₂. A few years later, a study of the electrochemical lithium deintercalation showed that several structural transitions occurred with, especially, the formation of the new O6-type phase.

Three years ago, this system was reinvestigated from the structural and physical properties point of view, a special interest being devoted to the NMR and electronic properties characterization. In the meantime, an *in-situ* XRD characterization study was reported by Paulsen and Dahn who confirmed to a large extent the previous results. Nevertheless, two very interesting points were found by these authors: (i) in the $0.5 < x < 0.7$ composition range, the XRD pattern gives evidence of the formation of a new oxygen packing which was characterized in the case of the Li_{2/3}Ni_{1/3}Mn_{2/3}O₂ phase, (ii) the O2-type packing is regenerated at the very end of the lithium deintercalation.

In our study, the P2-Na_{0.70}CoO₂ precursor and the O2-LiCoO₂ phase were characterized by Rietveld refinement of the X-ray and neutron diffraction patterns. In the O2 packing, the lithium ions occupy only the octahedral sites, even if these sites share faces with the CoO₆ octahedra. The magnetic properties and ⁷Li NMR studies show that the O2-type phase exhibits a composition very close to the ideal one with only low spin trivalent cobalt ions. Moreover, the O3-type LiCoO₂ phase obtained after thermal treatment of O2-LiCoO₂ presents the ideal structure without any trace of the defects related to a Li:Co ratio slightly larger than one. A comparative ⁵⁷Co and ⁷Li MAS NMR study of the two varieties of LiCoO₂ shows that the Electrical Field Gradient (EFG) at the cobalt site is three times larger in the O2 variety as in the O3 one, as a result of the CoO₆-LiO₆ face sharing in the O2 type phase.

Electrochemical lithium deintercalation shows a very good reversibility in the overall composition range. Several structural transitions occur. For $0.5 < x < 0.7$, the T[#]2-type phase is obtained. The structure of this material is very similar to that of the Li_{2/3}Ni_{1/3}Mn_{2/3}O₂ phase recently reported by Paulsen and Dahn. The T[#]2 notation is used instead of the T2 one, proposed by these authors, in order to avoid any confusion in the oxygen packing, since, in the T[#]2-type phase, the oxygen atoms do not occupy, like in all other layered structures, the classical A,B,C positions of a triangular lattice. A neutron diffraction study shows that the lithium ions are in very distorted tetrahedral sites, but does not allow one to determine their accurate distribution. An electron diffraction study of the T[#]2 Li_xCoO₂ phase revealed evidence of superstructures. The existence of a very distorted site for lithium ions is emphasized

by the strong quadrupolar broadening of the ⁷Li MAS NMR signal.

The O6-type phase obtained in the $0.33 < x < 0.42$ composition range is characterized by XRD; Rietveld refinement shows the presence of two different CoO₆ slabs with slightly different thickness.

Although the electrochemical profile is very reproducible, the broadening of some specific XRD peaks of deintercalated Li_xCoO₂ was related to the electrode technology and cycling conditions. We believe that this behavior is attributed to the formation of stacking faults associated to various slab gliding processes. The modification of the structurally related physical properties upon lithium deintercalation is studied by electronic conductivity, thermopower measurements and by ⁷Li MAS NMR. Similar to the O3-type Li_xCoO₂ system, the electrons remain localized at the very beginning of the lithium deintercalation ($0.97 \leq x \leq 1$). For the T[#]2 and O6-type phases, metallic properties are clearly evidenced, with the formation of holes in the broad t₂ electronic band.

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